PATENT SPECIFICATION

(11) **1 447 419**

1 447 419

(21) Application No. 15719/74 (22) Filed 9 April 1974
(31) Convention Application No. 42403/73
(32) Filed 14 April 1973 in
(33) Japan (JA)
(44) Complete Specification published 25 Aug. 1976
(51) INT CL^2 C08L 53/02, 57/02; C09J 7/02, 7/04//(C08L 53/02, 57/02); (C08L 57/02, 53/02)
(52) Index at acceptance
C3P 102 12D1 3D 3K2 3K7 7D2A1 7K11 7K2 E2 PC12X PC13B
B2E 185 18Y 19Y 204 207 209 20Y 226 22Y 23Y 246 24Y 299 319 339 349 398 421 42X 435 439 43Y 44Y 47X 492 493 49Y 508 510 51X 520 533 535 536 53Y 545 546 547 54Y 555 557 55Y

(19) THE PATENT OFFICE LONDON

(54) HOTMELT PRESSURE SENSITIVE ADHESIVE COMPOSITION

(71) We, ARAKAWA RINSAN KAGAKU KOGYO KABUSHIKI KAISHA, a Japanese corporate body, of 21, 1-chome, Hiranomachi, Higashi-ku, Osaka-shi, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel hotmelt pressure sensitive adhesive composition, more particularly to an adhesive composition which is applicable to a tape, sheet or like base material in molten state and which exhibits pressure sensitive adhesive properties when cooled.

In view of the health of workers and pollution control, attention has been formed, in recent years, on pressure sensitive adhesives of the hotmelt type containing no solvent.

As already known, pressure sensitive adhesives must be excellent in the three adhesive properties of tackiness, adhesion and cohesion. Furthermore with those of the hotmelt type which are applied to the base material in molten state, the adhesives must be free of coloration when melted and must have excellent stability against aging so that the adhesive after application to the base material in molten state, will not be degraded with the lapse of time in any of the above-mentioned three adhesive properties.

However, these requirements have not been fulfilled by conventional pressure sensitive adhesives of the hotmelt type. For example, block copolymers prepared by the anionic copolymerization of diene polymers such as polyisoprene, polybutadiene, etc. and polyvinyl arenes such as polystyrene are proposed for use as the elastomer ingredient of hotmelt pressure sensitive adhesives. The proposal has aroused interest since the block copolymers have outstanding cohesion and thermoplasticity. However, the block copolymers are low in compatibility with terpene, resins, glycerin esters or rosin, glycerin esters of hydrogenated rosin, pentaerythritol esters of hydrogenated rosin, coumarone-indene resins, petroleum resins and like known tackifiers, with the result that the composition of two ingredients of the above-mentioned block copolymer and tackifier has extremely low tackiness and is not usable in practice. It therefore becomes necessary to improve the compatibility of the block copolymer with the tackifer and to impart greater tackiness to the composition by using an extender oil conjointly with the block copolymer which extender oil is compatible with the polyvinyl arene constituent of the block copolymer but compatible with the diene polymer as described in U.S. Patent No. 3,239,478, whereas the use of such extender oil reduces cohesion, the characteristic property of the block copolymer and adversely affects the stability of the composition after it has been applied to the base material.

Reference is herein made to our prior U.K. Patent Specification No. 1,176,443 which describes a pressure-sensitive adhesive which comprises one or more natural or synthetic rubbers and a hydrogenated hydrocarbon resin tackifier.

This invention provides a hotmelt pressure sensitive adhesive composition containing a block copolymer as its elastomer ingredient and excellent in the three adhesive properties of tackiness, adhesion and cohesion notwithstanding that the composition does not contain an extender oil, the composition thus being free from the foregoing drawbacks due to the use of extender oil.

This invention further provides a hotmelt pressure sensitive adhesive which is free of coloration when melted.

This invention further provides a hotmelt pressure sensitive adhesive which is free of aging after it has been applied to the base material.

The hotmelt pressure sensitive adhesive composition of the present invention comprises:

(a) a block copolymer having the general formula

A—B or A—B—A

wherein A is a homopolymer of a vinyl arene or a copolymer of two or more vinyl arenes having an average molecular weight of from 5,000 to 125,000, B is a homopolymr of a conjugated diene or a copolymer of two or more conjugated dienes, which may be hydrogenated, having an average molcular weight of from 15,000 to 250,000, and the content of the polymer block represented by B is at least 20% by weight, and

(b) a hydrogenated aromatic petroleum resin, present in an amount of from 30 to 300 parts by weight, based on 100 weight parts of the block copolymer, prepared by polymerizing a cracked petroleum fraction boiling at a temperature within the range of from −10 to 280°C. and containing polymerizable unsaturated hydrocarbons, at least 50% by weight of which are polymerizable aromatic hydrocarbons, and hydrogenating the resulting aromatic hydrocabon resin to a hydrogenation degree of aromatic ring, as herein defined, of from 30 to 100%. The "hydrogenation degree of aromatic ring" or "hydrogenation degree" referred to herein is determined by the following equation based on the infrared absorbancy at 700 cm^{-1}.

$$\text{HYDROGENATION DEGREE OF AROMATIC RING (\%)} = \left(1-\frac{\text{ABSORBENCY AT } 700\text{cm}^{-1} \text{ OF PETROLEUM RESIN AFTER HYDROGENATION}}{\text{ABSORBENCY AT } 700\text{cm}^{-1} \text{ OF PETROLEUM RESIN BEFORE HYDROGENATION}}\right)\times 100$$

Our researches have revealed that the above-mentioned hydrogenated aromatic hydrocarbon resin has excellent compatibility with the block copolymer and that the composition prepared by mixing these two ingredients has outstanding properties as a hotmelt pressure sensitive adhesive in that it exhibits high tackiness, cohesion and adhesion in spite of the absence of any extender oil, is free of coloration or viscosity variations in molten state and does not undergo aging after application to the base material. We have conducted studies on various known tackifiers to find that they are all incapable of giving satisfactory tackiness when no extender oil is used and that the aforementioned specific hydrogenated aromatic hydrocarbon resin only exhibits such outstanding properties in the absence of extender oil.

The block copolymer to be used in this invention is represented by the general formula

A—B (I)

or

A—B—A (II)

in which A and B are the same as above and in the formula (II) polymer blocks A are those of the same or different vinyl arenes. The polymer block A has an average molecular weight of 5,000 to 125,000, preferably of 15,000 to 100,000, and preferably a glass transition temperature of at least 20°C. The monomers constituting the polymer block are one or at least two of styrene, methylstyrene, chlorostyrene, vinyl toluene, vinyl xylene, vinyl naphthalene and like vinyl arenes. Preferably polymer block A is polystyrene. The conjugated diene polymer block B has an average molecular weight of 15,000 to 250,000, preferably of 25,000 to 150,000. The glass transition temperature of the polymer block B is preferably at least 50°C, more preferably at least 100°C, lower than that of the polymer block A. The polymer block B is prepared from one or at least two of conjugated dienes such as butadiene, isoprene or piperylene. The amount of the polymer block B contained in the block copolymer must be at least 20% by weight and may preferably be in the range of 20 to 80% by weight. The block A and block B may be bonded together directly or with a suitable coupling agent such as dibromobutane or divinyl benzene.

The block copolymer may be hydrogenated partially or completely. Usually, the polymer block B in the block copolymer may be hydrogenated to ensure improved weather resistance.

Representative block copolymers are those having the formula (I) in which polymer block A is polystyrene and polymer block B is polybutadiene and those having the formula (II) in which each polymer block A is polystyrene and polymer block B is polybutadiene, polyisopropene or hydrogenated polyisoprene, the latter block copolymer (II) being the most preferable. Preferable block copolymers (I) are, for example, polystyrene-polybutadiene block copolymer and preferably block copolymers (II), are, for example, polystyrene-polybutadiene-polystyrene block copolymer, polystyrene-polyisoprene-polystyrene block copolymer and polystyrene-hydrogenated polyisoprene-polystyrene block copolymer. These copolymers are easily available under the trade marks of "Solprene 1205" (polystyrene-polybutadiene block copolymer of Phillips Petroleum Company, U.S.A.), "Cariflex TR—1102" (polystyrene-polybutadiene-polystyrene block copolymer of Shell Chemical Company, U.S.A.) "Cariflex TR—1107" (polystyrene-polyisoprene-polystyrene block copolymer of Shell Chemical Company, U.S.A.) and "Kraton GX—6500" (polystyrene-hydrogenated polyisoprene-polystyrene block copolymer of Shell Chemical Company, U.S.A.).

The block copolymer can be prepared by known methods, preferably by living polymerization known in the art. For example, vinyl arenes are polymerized in the presence of a lithium based initiator such as lithium metal, alkyl lithium or dilithium initiator to obtain a vinyl arene polymer having a specified molecular weight, and a conjugated diene is then added to the reaction system for polymerization to obtain a polyvinyl arene-polydiene block copolymer having the formula (I) of the desired molecular weight. When a block copolymer having the formula (II) is desired, a vinyl arene is further added to the resulting reaction system to effect polymerization and to thereby obtain a vinyl arene-diene-vinyl arene block copolymer having the desired molecular weight. Generally, the polymerization reaction is conducted in the presence of a polar or non-polar solvent. When it is desired to obtain a copolymer having a diene polymer block of high cis structure, isoprene is used as the diene and polymerization is effected in a non-polar solvent. If a more branched structure is desired, a polar solvent may be used. Where the polymerization system contains a suitable coupling agent, the polymer blocks A and polymer block B can be coupled together with the aid of the coupling agent.

The block copolymer described is an elastomer which *per se* has rubber-like elasticity and thermoplasticity and is soluble in organic hydrocarbon solvents such as cyclohexane, toluene, benzene, xylene, etc. Furthermore, it is possible to produce a block copolymer of the desired molecular weight in accordance with the reaction conditions. Thus the copolymer obtained is usable as it is unlike natural rubber which requires vulcanization and mastication.

According to the present invention, it is essential to use a hydrogenated product of specified aromatic petroleum resin. This makes it possible to obtain an excellent hotmelt pressure sensitive adhesive which contains the above-stated block copolymer as its elastomer component, without using an extruder oil.

The aromatic petroleum resin to be used in this invention is prepared from a petroleum fraction containing at least 50% by weight of polymerizable aromatic hydrocarbons based on the total weight of the polymerizable unsaturated hydrocarbons contained therein. The polymerizable aromatic hydrocarbons include aromatic hydrocarbons having a polymerizable double bond either on the side chain or in the condensed ring. Examples thereof are styrene, α-methyl styrene, vinyl toluene, vinyl xylene, propenyl benzene, indene, methyl indene, ethyl indene, etc. Usually the above starting fraction is obtained by cracking or reforming petroleum naphtha and boils in the range of −10 to 280°C, preferably −10 to 260°C. Such petroleum fractions may contain polymerizable unsaturated hydrocarbons other than polymerizable aromatic hydrocarbons. The polymerizable unsaturated hydrocarbons other than polymerizable aromatic hydrocarbons may include cyclic olefins and diolefins such as cyclopentene, cyclopentadiene, dicyclopentadiene, cyclohexene, cyclooctene, etc., and aliphatic olefins and diolefins such as butene, butadiene, isoprene, pentene, pentadiene, octadiene, etc. The fraction may further contain paraffins, alkylbenzenes and the like non-polymerizable substances.

The above fraction may be polymerized by conventional methods. In one of the preferred methods, the polymerization is carried out in an organic solvent in the presence of a radical catalyst or Friedel-Crafts catalyst, generally at −50 to 100°C under atmospheric or increased pressure for 2 to 8 hours. The resultant resin from which the catalyst and solvent are removed is in oily to mass form, colorless or brown in color. Preferably the resin is a liquid or a solid having a softening point of up to 130°C, although the physical properties can be varied by the starting fraction used and polymerization conditions.

According to this invention, the aromatic petroleum resin is then hydrogenated. The hydrogenation degree exerts an important effect on the compatibility with the block copolymer and tackiness and adhesion of the resulting composition. According to this invention, it is essential that the aromatic rings be hydrogenated to a hydrogenation degree of 30 to 100%. We have found that marked improvement in the compatibility with the block copolymer is assured at a hydrogenation degree of from 30 to 100%. If the degree is below 30%, the resin will exhibit greatly reduced compatibility with the block copolymer and low tackiness and adhesion, possibly causing the resulting composition to undergo colouration and variations in viscosity when melted. Thus, only when hydrogenation is effected to a hydrogenation degree of 30 to 100%, the resulting resin shows excellent compatibility with the block copolymer and gives a hotmelt pressure sensitive adhesive composition having excellent tackiness, adhesion and cohesion. The preferable hydrogenation degree of aromatic ring depends on the kind of the block copolymer used. For example, a hydrogenation degree of 30 to 80%, more particularly 50 to 80%, is preferably for polystyrene-polybutadiene-polystyrene block copolymer. 50 to 100% is preferable for polystyrene-polyisoprene-polystyrene block copolymer and 80 to 100% is preferable for hydrogenated block copolymer of polystyrene-polyisoprene-polystyrene.

The method of hydrogenation is not particularly limited but conventionally known methods may be adopted. For instance, the hydrogenation may be carried out at a temperature of 150 to 300°C and pressure between 10 and 300 kg/cm^2 in the presence of a known hydrogenating catalyst such as nickel, palladium, cobalt, ruthenium, platinum, rhodium, the conditions being such that they permit the production of resins with a hydrogenation degree of 30 to 100%. The amount of catalyst to be used is usually in the range of 0.05 to 20 parts by weight, based on 100 weight parts of the resin used. The hydrogenation reaction generally is completed within 0.5 to 10 hours.

Preferable as the hydrogenated resins are those in the form of a liquid at room temperature and having boiling points of not lower than 300°C and those in the form of a solid at room temperature and having softening points of not high than 125°C. Especially preferable are those having a softening point of 20 to 70°C, most preferably 30 to 60°C. The liquid resin is preferably used in admixture with solid resin.

The hotmelt pressure sensitive adhesive composition of this invention is prepared by mixing the block copolymer and hydrogenated aromatic petroleum resin with a Banbury's mixer or mixing roll and melting the resulting mixture preferably at a temperature of from 120 to 200°C. The ratio between these two components is 30 to 300 parts by weight, preferably 50 to 250 parts by weight, of the latter per 100 parts by weight of the former. Synthetic rubbers such as random SBR, polyisobutylene, etc. and ethylene-vinyl acetate copolymer can be conjointly employed with the block copolymer. Further employable with the hydrogenated aromatic petroleum resin are known tackifiers such as hydrogenated rosin, polyterpene resins, glycerin esters of hydrogenated rosin, pentaerythritol esters of hydrogenated rosin, methyl esters of hydrogenated rosin, higher alcohol esters of hydrogenated rosin, etc. However, these additional ingredients must be used in such amounts that they will not degrade the tackiness, adhesion, cohesion and stability against aging of the composition obtained. The composition of this invention need not have incorporated therein any extender oil which has heretofore been used as an essential ingredient, whereas, as in the conventional practice, the composition may contain various additives such as antioxidant for preventing the oxidation of the composition and a plasticizer for lowering the melt viscosity. These additives should also be used in such amounts that they will not deteriorate the properties of the composition.

The pressure sensitive adhesive composition of this invention is applied, in molten state, to various base materials which are in a sheet-like form such as film and sheet. Examples of the sheet-like base materials are paper, plastic film, plastic sheet, woven fabric, nonwoven fabric, wood plate, metal plate, glass plate, rubber sheet, synthetic paper, tape, tile, laminate, etc. The preferable melting temperature of the composition is usually from 120 to 200°C. Advantageously usable are compositions having melt viscosities of 10,000 to 230,000 cps. Usually, the molten composition is applied to the surface of base material by an applicator, roll coater or like coating means and is then cooled. The coating may usually have a thickness of 10 to 500 microns. Alternatively, the base material is continuously passed through a molten composition, whereby coatings are formed on the surfaces and subsequently cooled. Similarly various other known applicating method are employable. For example, the present composition may be extruded in molten state to produce a film or sheet, on one or both surface of which is adhered releasing paper.

For a better understanding of the invention examples are given below.

Example 1.

By steam cracking of petroleum naphtha, a hydrocarbon fraction was obtained which had a boiling point of 130 to 240°C and contained 52 wt. % of styrene, indene and their polymerizable derivatives, 39 wt. % of non-polymerizable aromatics, 3 wt. % of olefin, less than 1 wt. % of diolefin and 5 wt. % of paraffin and naphthene. To 1,000 g of the hydrocarbon fraction was added 300 g of hydrocarbons consisting of 58 wt. % of olefin and 42 wt. % of paraffin and obtained by removing diolefin from a hydrocarbon fraction boiling at −10 to 15°C. To the mixture was added 13 g of boron trifluoride-phenolate as a catalyst, and the mixture was then polymerized at a temperature of 30°C for 3 hours. To the resulting reaction mixture was added a 10 wt. % aqueous sodium hydroxide solution and then the mixture was heated at a temperature of 80°C under an atmospheric pressure.

After the aqueous phase was separated off, the reaction mixture was washed with hot water at 50°C three times and was thereafter heated to 180°C under a reduced pressure of 5 mm Hg to remove unreacted substances and low polymers. As a result, 480 g of a hydrocarbon resin having a ball and ring softening point of 55°C was obtained. The resin will be referred to as Sample resin 1 hereinafter.

100 g of the aromatic petroleum resin thus obtained and 100 g of cyclohexane were dissolved in an autoclave to prepare a solution, which was then heated to 200°C and at hydrogen pressure of 200 kg/cm^2 in the presence of 8 g of Raney nickel catalyst for 2 hours. After the reaction, the catalyst was removed by passing the resulting hydrogenated solution through a glass filter. Subsequently, cyclohexane was distilled off from the solution to obtain 100 g of a hydrogenated resin having a hydrogenation degree of 12% and a softening point of 55°C. The resin will be referred to as Sample resin 2.

In the same manner as above, hydrogenated resins having different hydrogenation degrees and softening points were prepared from Sample resin 1 by varying the kind and amount of catalyst, hydrogen pressure, reaction temperature and time as listed in Table 1 below, each hydrogenated resin thus obtained being hereinafter referred to as Sample resin 3, 4, 5, 6 or 7 as shown in Table 1.

TABLE 1.

Sample resin No.	Catalyst		Reaction Temp. (°C)	Reaction time (h)	Hydrogen pressure (kg/cm²)	Yield (%)	Softening point (°C)	Hydrogenation degree (%)
	Kind	Amount (g)						
1							55	0
2	Raney nickel	8	200	2	5	100	55	12
3	Nickel-diatomaceous earth	1	200	5	50	97	53	35
4	Stabilized nickel-diatomaceous earth	1.5	250	5	150	98	52	52
5	Stabilized nickel-diatomaceous earth	2	250	5	150	95	52	70
6	Stabilized nickel-diatomaceous earth	5	250	5	150	95	50	80
7	Stabilized nickel-diatomaceous earth	10	250	5	150	90	50	100

100 g of commercial polystyrene-polybutadiene-polystyrene block copolymer (trade mark: "Cariflex TR—1102", product of Shell Chemical Company, U.S.A.) and 140 g of Sample resin 4 were mixed together, and 1 g of zinc di-n-butyldithiocarbamate (antioxidant) was further added. The resulting mixture was mixed at 120°C and then heated to 180°C to prepare an adhesive composition having a melt viscosity of 40,000 to 60,000 cps. In the same manner as above, similar compositions were prepared using Sample resins 3, 5 and 6 listed in Table 1. Likewise, Sample resins 1 to 2 and glycerin ester of hydrogenated rosin, pentaerythritol ester of hydrogenated rosin, terpene resin and 2-methyl-2-butene-piperylene resin were used to prepare like compositions for comparison.

Each of the compositions was applied, at the same temperature as above, to a polyester film (trade mark: "Lumirror", product of Toray Industries, Inc., Japan) to a thickness of 150 μ by an applicator to prepare a pressure sensitive adhesive tape. The tape was then cooled at 20°C, left to stand for 12 hours and then tested at 20°C for tackiness, adhesion and cohesion, with the results given in Table 2 below.

Furthermore after the application of the composition, the adhesive tape was left to stand at 70°C for 3 days in an air oven and thereafter maintained at 20°C for 12 hours. The tape was then similarly tested to determine degradation due to aging. The results are given in parentheses in Table 2.

The properties of the adhesive tape were determined by the following methods as specified by Pressure Sensitive Tape Council (PSTC).

Tackiness:

A polyester film, 25 mm x 300 mm, was coated with the adhesive composition by an applicator, and the tape obtained was tested to measure tackiness in accordance with the method of PSTC—6. The polyester film was placed on a horizontal plate, with the coated surface up, and another plate was placed at one end of the polyester film so as to extend upward obliquely at an angle of 30°. with the horizontal plate. a steel ball 10 mm is diameter was rolled down the oblique plate from a position 10 cm from the bottom of the plate, and the distance the steel ball rolled along on the adhesive surface of the polyester film was measured. The smaller the measured value, the better is the result.

Adhesion:

A polyester film, 15 mm in width, was coated with the adhesive composition by an applicator to prepare an adhesive tape. As specified under PSTC—1, the tape was adhered to a stainless steel panel, and the panel was placed on a Tensilon (Registered Trade Mark) tester, UTM—III model (manufactured by Toyo Measuring Instruments Co., Ltd., Japan) and subjected to a peeling test at an angle of 180° at 300 mm/min to measure the load required for peeling.

Cohesion:

A polyester film, 15 mm in width, was coated with an adhesive composition to prepare an adhesive tape. The test piece was adhered to a glass panel over an area of 15 mm x 5 mm, and the panel was placed on the same Tensilon tester as above and subjected to shearing tension test at a constant rate of 5 mm/min. When the adhered test piece was displaced from the original place on the glass panel, the load required therefor was measured.

TABLE 2.

Sample No.	Hydrogenation degree (%)	Softening point of hydrogenated product (°C)	Tackiness (cm)		Adhesion (g/15 mm)		Cohesion (g/15x5 mm²)	
1	0	55	none	(none)	—	(—)	—	(—)
2	12	55	above 30	(none)	500	(—)	800	(—)
3	35	53	15	(25)	800	(300)	1000	(1500)
4	52	52	6.5	(14)	1300	(700)	1800	(2200)
5	70	52	4.5	(10)	1500	(900)	2000	(2300)
6	80	50	6.2	(10)	1400	(900)	2000	(2250)
A	Glycerin ester of hydrogenated rosin	70	above 30	(none)	2500	(—)	1500	(—)
B	Pentaerythritol ester of hydrogenated rosin	95	above 30	(none)	1500	(—)	2000	(—)
C	Terpene resin	70	none	(none)	—	(—)	—	(—)
D	2-Methyl-2-butenepiperylene resin	95	none	(none)	—	(—)	none	(—)

Note: The symbol "—" indicates that the property was undeterminable, as in the tables to follow.

Example 2.

To 100 g of a commercial polystyrene-polyisoprene-polystyrene block copolymer (trade mark: "Cariflex TR—1107", product of Shell Chemical Company, U.S.A.) was added 140 g of the hydrogenated resin prepared in Example 1, followed by the same procedure as in Example 1 to prepare a pressure sensitive adhesive tape. As listed in Table 3 below, the tackiness, adhesion and cohesion of seven kinds of tapes thus prepared were measured, along with their stability against aging (given in parentheses). These properties were determined in the same manner as in Example 1.

TABLE 3.

Sample No.	Hydrogenation degree (%)	Softening point of hydrogenated product (°C)	Tackiness (cm)		Adhesion (g/15 mm)		Cohesion (g/15×5 mm²)	
1	0	55	above 30	(none)	1850	(—)	3200	(—)
2	12	55	above 30	(above 30)	1790	(—)	3000	(—)
3	35	53	12.6	(26)	1640	(1850)	2450	(3000)
4	52	52	8.0	(20.0)	1580	(1200)	2000	(2500)
5	70	52	5.0	(15.0)	1550	(1300)	1950	(1900)
6	80	50	5.4	(13.4)	1510	(1320)	1920	(1940)
7	100	50	5.5	(10.2)	1550	(1410)	1900	(2000)

Example 3.

100 g of commercial polystyrene-hydrogenated polyisoprene-polystyrene block copolymr (polystyrene-ethylenepropylene copolymer-polystyrene block copolymer) (trade mark: "Kraton GX—6500", product of Shell Chemical Company, U.S.A.) and 140 g of the hydrogenated resin obtainable in Example 1 were mixed together, and 1 g of zinc di-n-butyl dithiocarbamate was added. The mixture was then mixed and melted at 180°C to prepare an adhesive composition. For comparison, similar compositions were prepared in the same manner as above using unhydrogenated resin, resin having hydrogenation degree of 12% and tackifiers of glycerin ester of hydrogenated rosin, pentaerythritol ester of hydrogenated rosin and terpene resin, respectively.

Using an applicator, each of the compositions was applied to a polyester film to a thickness of 250 μ to obtain an adhesive sheet, which was left to stand overnight at 20°C and thereafter tested for tackiness, adhesion and cohesion.

The tackiness was measured on a Polyken Probe Tack Tester (product of Kendal Company, U.S.A.) under the conditions of:

Probe diameter	5 mm
Contact pressure	10 g/cm^2
Contact time	0.2 sec.
Separation rate	5 cm/sec.

The greater the measured value, the better is the result.

The adhesion and cohesion were determined in the manner as in Example 1. The results are given in Table 4 below.

TABLE 4.

Sample No.	Hydrogenation degree (%)	Softening point of hydrogenated product (°C)	Tackiness (g/cm^2)	Adhesion (g/15 mm)	Cohesion (g/15×5 mm^2)
1	0	55	none	—	—
2	12	55	none	—	—
3	35	53	70	1600	4000
4	52	52	100	3000	3500
5	70	52	180	2800	2800
6	80	50	400	2400	2100
7	100	50	600	1800	1400
A	Glycerin ester of hydrogenated rosin	70	none	—	—
B	Pentaerythritol ester of hydrogenated rosin	95	none	—	—
C	Terpene resin	70	none	—	—

Example 4.

With agitation and water-bath cooling, 120 g of boron trifluoride ethereate was added dropwise to 12 kg of a fraction boiling in the range of 140 to 200°C obtained by thermal cracking of petroleum naphtha. The starting fraction consisted of 38 wt. % of styrene, indene and their polymerizable derivatives, 47 wt. % of non-polymerizable aromatic compounds and 15 wt. % of other non-polymerizable substances. The mixture was continuously agitated for a further three hours at about 25°C after the termination of heat generation. 1 liter of a 5 wt. % aqueous solution of caustic soda was thereafter added to the mixture, followed by vigorous agitation for 1 hour to decompose the catalyst. The resulting aqueous phase was separated off. The product obtained was subsequently washed with water three times and then distilled to give 5.1 kg of a mass of aromatic hydrocarbon resin of brown color as a residue. The resin had a ball and ring softening point of 124°C.

500 g of the aromatic petroleum resin thus obtained was dissolved in the same amount of decalin, and the solution was heated in an autoclave under a hydrogen presure of 150 kg/cm^2 at a temperature of 300°C for 8 hours in the presence of 20 g of nickel-diatomaceous earth catalyst to prepare 400 g of hydrogenated resin having a softening point of 54°C and hydrogenation degree of 100%.

To 100 g of a commerical polystyrene-hydrogenated polyisoprene-polystyrene block copolymer (trade mark: "Kraton GX—6500", the same as in Example 3) was added 140 g of the above hydrogenated resin, and 1 g of zinc di-n-butyl dithiocarbamate was further added. The mixture was mixed and melted at 180°C to obtain a composition having a melt viscosity of 200,000 cps at 180°C. The composition was applied by an applicator to a polyester film to a thickness of 250 μ at the same temperature to prepare an adhesive sheet, which was then cooled to 20°C and left to stand overnight. In the same manner as in Example 3, the thickness, adhesion and cohesion of the sheet were measured, with the results shown below.

Tackiness (g/cm^2)	580
Adhesion (g/15 mm)	1,900
Cohesion (g/15 x 5 mm^2)	1,600

Example 5.

To 100 g of a commercial polystyrene-polybutadiene block copolymer (trade mark: "Solprene 1205", product of Phillips Petroleum Company, U.S.A.) was added 100 g of Sample resin-5 having a hydrogenation degree of 70%, and 1 g of zinc di-n-butyl-carbamate was further added. The mixture was mixed at 120°C and further at 180°C to obtain a pressure sensitive hotmelt composition having a melt viscosity of .60,000 cps at 180°C.

WHAT WE CLAIM IS:—

1. A hotmelt pressure sensitive adhesive composition, which comprises:

(a) a block copolymer having the general formula

A—B or A—B—A

wherein A is a homopolymer of a vinyl arene or a copolymer of two or more vinyl arenes having an average molecular weight of from 5,000 to 125,000, B is a homopolymer of a conjugated diene or a copolymer of two or more conjugated dienes, which may by hydrogenated, having an average molecular weight of from 15,000 to 250,000 and the content of the polymer block represented by B is at least 20% by weight, and

(b) a hydrogenated aromatic petroleum resin, present in an amount of from 30 to 300 parts by weight, based on 100 weight parts of the block copolymer, prepared by polymerizing a cracked petroleum fraction boiling at a temperature within the range of from −10 to 280°C and containing polymerizable unsaturated hydrocarbons, at least 50% by weight of which are polymerizable aromatic hydrocarbons, and hydrogenating the resulting aromatic hydrocarbon resin to a hydrogenation degree of aromatic ring, as herein defined, of from 30 to 100%.

2. A hotmelt pressure-sensitive adhesive composition according to claim 1, in which the block copolymer has the general formula

A—B

and A is polystyrene and B is polybutadiene.

3. A hotmelt pressure-sensitive adhesive composition according to claim 1, in which the block copolymer has the general formula

A—B—A

and A is polystyrene and B is polybutadiene, polyisoprene or hydrogenated polyisoprene.

4. A hotmelt pressure-sensitive adhesive composition according to Claim 1, in which the block copolymer is a polystyrene-polybutadiene-polystyrene block copolymer and the hydrogenation degree of the hydrogenated armatic petroleum resin is from 30 to 80%.

5. A hotmelt pressure-sensitive adhesive composition according to Claim 4, in which the hydrogenation degree is from 50 to 80%.

6. A hotmelt pressure-sensitive adhesive composition according to Claim 1, in which the block copolymer is a polystyrene-polyisoprene-polystyrene block copolymer and the hydrogenation degree of the hydrogenated aromatic petroleum resin is from 50 to 100%.

7. A hotmelt pressure-sensitive adhesive composition according to Claim 1, in which the block copolymer is a polystyrene-hydrogenated polyisoprene-polystyrene block copolymer and the hydrogenation degree of the hydrogenated aromatic petroleum resin is from 80 to 100%.

8. A hotmelt pressure-sensitive adhesive composition according to Claim 1, in which the hydrogenated aromatic petroleum resin is present in an amount of from 50 to 250 parts by weight, based on 100 weight parts of the block copolymer.

9. A pressure-sensitive adhesive sheet-like material which comprises a sheet-like base material having thereon a coating of the composition claimed in Claim 1.

10. A hotmelt pressure-sensitive adhesive composition according to claim 1 and substantially as herein described in any of the Examples.

A. A. THORNTON & CO.,
Chartered Patent Agents,
Northumberland House,
303/306 High Holborn,
London, W.C.1.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1976.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.